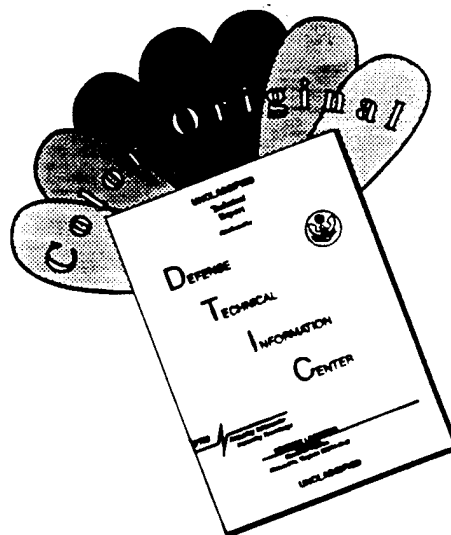


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13. ABSTRACT (Maximum 200 words) Using a Variable frequency Microwave Furnace (VFMF) technology, Lambda Technologies has demonstrated the ability to tune to the optimum incident frequency for best coupling into a given material structure (e.g., polymer matrix composite, PMC), and then by sweeping around that incident center frequency, producing uniform energy distribution throughout the cavity and sample volume. Hence, the advantages of microwave energy---enhanced reaction rates, reduced process time, and heat generation at the molecular level---are now obtainable with controlled and uniform results compatible for commercial scale-up. The processing via VFMF is 8 - 10 times faster than conventional processing methods. The advantages of VFMF technology over single frequency microwave technology in achieving the uniform electromagnetic energy distribution required for rapid and reliable processing of advanced polymer composites are systematically demonstrated in the Phase I (Both Glass and Carbon fiber reinforced PMC were investigated). In addition, a numerical modeling program implemented during Phase I provided a foundation for the ability to predict field distribution and temperature profiles in various geometries (plate, disk and cylinder) and materials (glass and graphite fiber reinforced PMCs) when being heated				
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Microwave solutions for the next generation in advanced materials processing

Final Technical Report 0002AG
Contract: F49620-94-0069

**Development of a Variable Frequency Microwave Processing System
For Post Curing of Thermoset Polymer Matrix Composite Materials**

SBIR Phase I - Air Force Office of Scientific Research
by Lambda Technologies, Inc.
P.O. Box 31207, 8600 Jersey Court, Suite C
Raleigh, NC 27622

(1) Technical Objectives of Phase I Research:

- A. Evaluate the microwave heating characteristics of isocyanate/epoxy system thermoset PMC's as a function of frequency (center frequency and bandwidth), applied power level, and volume of processed material.
- B. Evaluate the material properties of variable frequency microwave processed thermoset PMC's to ensure their equivalence to those of conventionally processed thermoset PMC's.
- C. Develop and optimize a microwave-based post-curing process for thermoset PMC's.
- D. Using the above process, demonstrate uniform heating of thermoset PMC plates of overall dimensions: 20 cm x 20 cm by (at least) 7.5 mm thick, using Variable Frequency Microwave Furnace (VFMF).

In addition to these objectives, variable frequency curing of **graphite fiber reinforced epoxy** has been performed.

(2) Status of the research effort:

A. General Overview -

Using a Variable Frequency Microwave Furnace (VFMF) technology, Lambda Technologies has demonstrated the ability to tune to the optimum incident frequency for best coupling into a given material structure (e.g. polymer matrix composite, PMC), and then by sweeping around that incident center frequency, producing uniform energy distribution throughout the cavity and sample volume. **Hence, the advantages of microwave energy—enhanced reaction rates, reduced process time, and heat generation at the molecular level—are now obtainable with controlled and uniform results compatible for commercial scale-up. The processing via VFMF is 8 -10 time faster than conventional processing methods.**

The advantages of VFMF technology over single frequency microwave technology in achieving the uniform electromagnetic energy distribution required for rapid and reliable processing of advanced polymer composites are systematically demonstrated in the Phase I (Both Glass and Carbon fiber reinforced PMC were investigated). In addition, a **numerical modeling** program implemented during Phase I provided a foundation for the ability to predict field distribution and temperature profiles in various geometries (plate, disk and cylinder) and materials (glass and graphite fiber reinforced PMCs) when being heated with variable frequency microwave energy.

In addition to rapid and uniform processing and numerical modeling, Lambda Technologies has been involved in analyzing various advanced materials using variable frequency energy to perform **nondestructive verification of cured properties**. This technique was applied to the composites investigated in Phase I and **in-situ monitoring of cure** was demonstrated.

In response to a request by the contracting officer at the AFOSR, Lambda Technologies has prepared a Phase II proposal that will be submitted by May of this year. Lambda has established contacts with interested industrial

06 JUN 1995

partners during the Phase I program, three of which will be teaming up with Lambda for the phase II program. The Phase II development program will build on the successful results of the Phase I effort for applying an advanced microwave technique to process defense oriented glass and graphite fiber reinforced thermoset polymer matrix composites. The Phase II program includes two primary partners, Hughes Corp. and AutoAir, the end users who will provide technical CFC product direction, analysis of results, and final economic assessment. A third partner, EniChem, will be included in the Phase II team for a commercial, non defense-oriented, application. Under the Phase II effort, Lambda Technologies will develop optimized process cycles for our partner's end products while simultaneously developing the intelligent process control techniques for *in-situ* diagnostics.

B. Materials processing and Characterization-

A VFMF system was instrumented with Luxtron microwave transparent temperature probes. This system was successfully used to process numerous samples under a variety of processing conditions. Thermal profiles as a function of processing conditions (central frequency, bandwidth and sweep rate) have been derived. The glass transition, flex modulus, flex strength and the dielectric properties of the samples processed via variable frequency irradiation have been measured. The evaluation of microwave heating characteristics has been performed on a variety of sample sizes and configurations. Comparison between microwave and conventional processing and between variable frequency and fixed frequency microwave processing were performed. 2-D numerical modeling was performed on a variety of sample materials and sample dimensions. Numerical simulations for both fixed and variable frequency irradiation were performed. The possibility of *in-situ* monitoring of cure was demonstrated by Lambda Technologies. Lambda's concept of *in-situ* monitoring of cure was applied to some of the materials used in the Phase I study. All the objectives of Phase I were successfully achieved, the experimental work has been reported in the progress reports, and the major results are summarized as follows:

1. The processing time for the postcure of EniChem isocyanate/epoxy composites was reduced from 8 hours with the conventional thermal method to 50 minutes with the variable frequency microwave approach. (see Figure 1).
2. Batch process of ten (10) 5 cm x 5 cm square samples has been successfully carried out. The glass transition temperatures were measured throughout the batch configuration. The Tg values are relatively uniform for all samples (refer to Figure 2 and Table 1).
3. Post-cure of 20 cm x 20 cm samples was also successfully implemented in the laboratory scale variable frequency microwave system (see Figure 3).
4. Flex modulus, strength and impact strength of fully microwave post-cured composites were measured and properties were found to be equivalent when compared to those of conventionally-cured samples. The impact strength is 5.7 KJ/m² for both microwave and thermally postcured composites. The flex modulus and strength for VFMF postcured composites are 5.77 ± 0.15 (GPa) and 197 ± 15.5 (Mpa), respectively, while the flex modulus and strength for thermally postcured composites are 5.75 ± 0.14 (GPa) and 195 ± 11.5 (Mpa), respectively.
5. Glass transition temperatures (Tg) of the postcured samples were measured and results show that the composites were fully cured (i.e. have a Tg value of 258°C or more) and uniform throughout.
6. Glass transition temperatures of post-cured samples were studied as a function of the microwave processing conditions (see Figure 4). A full cure was achieved when the curing temperature exceeded 230°C during microwave heating. The effects of heating rate on the Tg's of microwave postcured PMCs were not significant. Tg analysis shows that the curing (crosslinking) resumed at 180°C during postcure (see Figure 5).
7. The dielectric constants and loss factors of cured and post-cured PMCs have been measured. The dielectric constants and loss factors increase with increasing temperatures until the temperature reached between 170 and 180°C then decrease with increasing temperature. The structural change occurring between 170 and 180 °C is caused by the onset of further curing--i.e., the formation of additional crosslinking. The curing resumption between 170 and 180 °C was confirmed by the Tg analysis. Thus, dielectric property measurements might be a good indication of the onset of post-curing. (see Figure 6).
8. The microwave depth of penetration was calculated over a range of temperatures and frequencies. The maximum thickness of this PMC material that can be uniformly processed using microwave irradiation is

50 cm. PMC samples of larger thickness will rely on their thermal conductivity characteristics to conduct heat to the interior. It is important to note that the dimensions (width and length) of PMC articles with thicknesses of less than 50 cm are not limited by this penetration depth (see Figure 7).

9. A Finite Difference Time Domain (FDTD) computer model was developed to simulate absorption and scattering in sample materials and cavity walls. The FDTD simulation predicts the location of hot spots and provides spatial heat source information within the sample, which are used to determine temperature and electric field profiles.
10. The FDTD model was used to simulate the E-field distribution inside a 8.65 cm x 8.65 cm sample when placed at the center of a 26x26 cm cavity when a single frequency, 2.45 GHz, microwave signal and when a microwave signal that is swept $\pm 10\%$ around 2.45 GHz are applied. The uniformity of the electric field was significantly improved by frequency sweeping. The calculated fields within the specimen at the fixed frequency contain large gradients, while the variable-frequency cavity simulation displays a uniform field within the specimen. (see Figure 8).
10. The temperature profiles generated within, 20 cm x 20 cm, glass reinforced isocyanate/epoxy composites during microwave irradiation were numerically modeled. Figures 9a and 9b illustrate the thermal gradients established within samples heated with fixed frequency and variable frequency. The temperature is uniformly distributed in the case of variable frequency.
11. The FDTD modeling result was confirmed by actual fixed and variable frequency processing of PMC plates. The results are shown in Figure 10.
12. Graphite fiber-reinforced epoxy composites were heated using the variable frequency microwave approach (see Figure 11.a and 11.b). Crossply composites tend to heat at a slower rate than unidirectional composites.
13. Several unidirectional graphite fiber-reinforced composites were heat treated under different experimental conditions. In general, carbon reinforced composites were found to heat efficiently at frequencies above 6.5 GHz. A typical thermal profile generated within carbon fiber composites is illustrated in Figure 12.
14. The T_g determinations using RDA techniques for the microwave heated samples are listed in Table 2. As illustrated in the Table, G' and G'' values (in dyn/cm²) are consistent throughout the investigated samples.
15. The materials' microwave absorption and dielectric properties (relative dielectric constant, relative loss factor and loss tangent) depend on the materials' extent of cure (refer to Figure 6). During variable frequency microwave irradiation one can derive a forward versus reflected power curve as a function of incident frequency for a variety of frequencies. This type of curves was found to exhibit characteristic peaks that can be traced to investigate the extent of cure of the material being irradiated. Figure 13 illustrates the shift of the characteristic peaks of an uncured and a fully cured epoxy resin ERL-2258 (Union Carbide) to which M-phenylenediamine hardener (Dupont) was added at the rate of 25 g MPDA per 100g resin. Figure 14 illustrates the forward versus reflected power curve for uncured and fully cured 8" x 8" PMC plates. As illustrated in Figures 13 and 14, the characteristic peaks of the materials under investigation change in position and/or magnitude during irradiation. This concept is being developed and will be incorporated as an integral part of an intelligent variable frequency microwave processing system.

(3) Technical Publications- The following publications on thermoset PMCs with variable Frequency microwave have been completed:

1. DeMeuse, M.T., and Johnson, A. C., "Microwave Processing of Thermoset PMCs", *Proceeding of the 1994 IMPI, Microwave Power Symposium*.
2. DeMeuse, M.T., and Johnson, A. C., "Variable Frequency Microwave Processing of PMCs", *MRS: Microwave Processing of Materials IV, 1994*.
3. Zak Fathi, Mark. T. DeMeuse, John Clemens and Craig Saltiel, "Processing and Modeling of Select PMCs using Variable Frequency Microwave Irradiation", *Spring 1995 ACS Conference*.
4. Zak Fathi, Mark. T. DeMeuse, John Clemens and Craig Saltiel, "Characterization & Numerical Modeling of Variable Frequency Microwave Processed Materials", *Spring 95 ACerS Conference*.

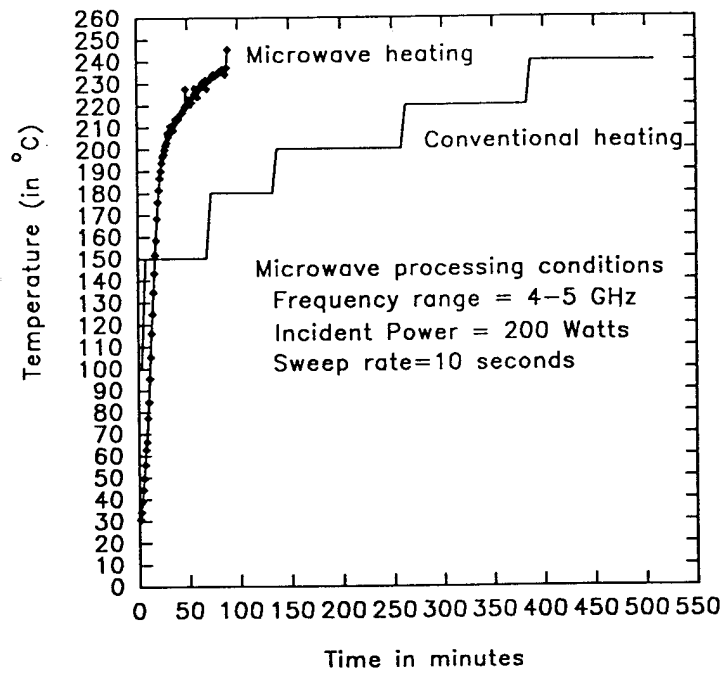


Figure 1 - Comparison of the recommended conventional and variable frequency processing cycles.

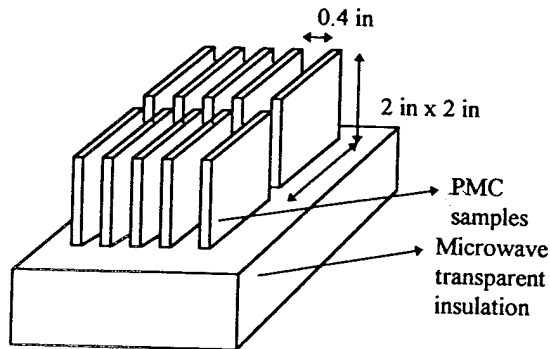


Figure 2- The variable frequency microwave batch process configuration.

Cure temperature (in °C)	T _g (in °C)	
230	248	243
"	261	263
"	263	262
"	255	260
"	250	258

Table 1- Glass transition values for PMC samples processed with variable frequency microwave energy.

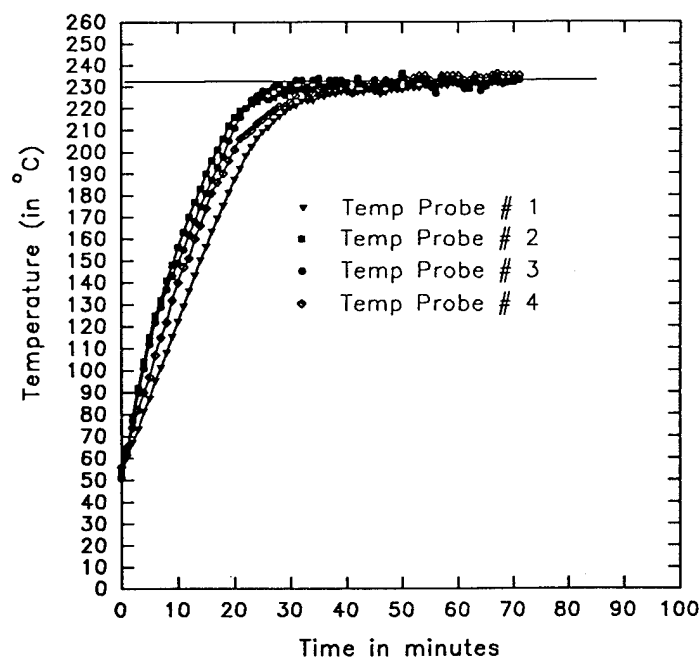


Figure 3- Temperature profiles obtained during variable frequency microwave processing of large (8 x 8 in²) PMC plates.

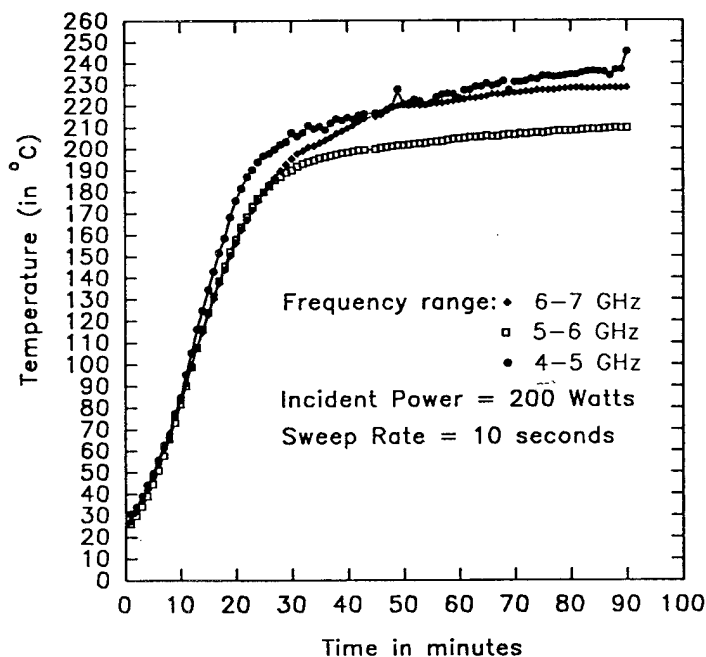


Figure 4- Thermal profiles of PMC samples irradiated with different frequencies.

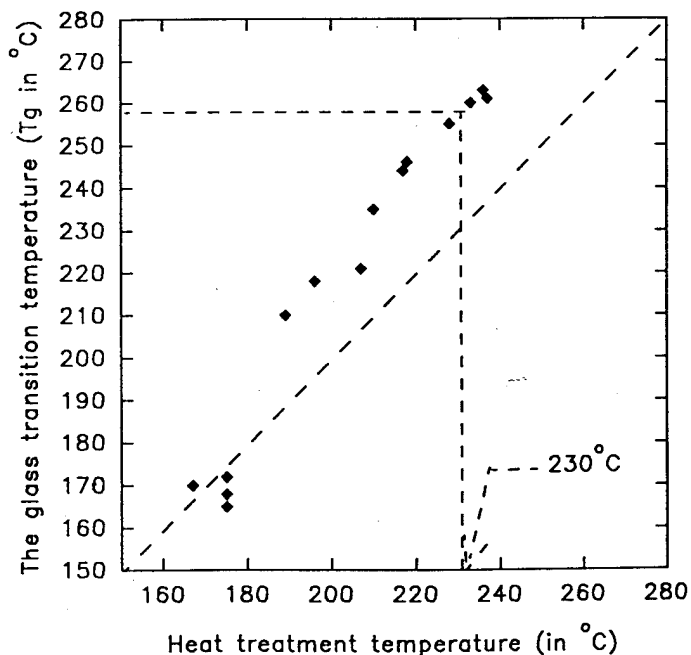


Figure 5- The glass transition of various samples as a function of the curing temperature.

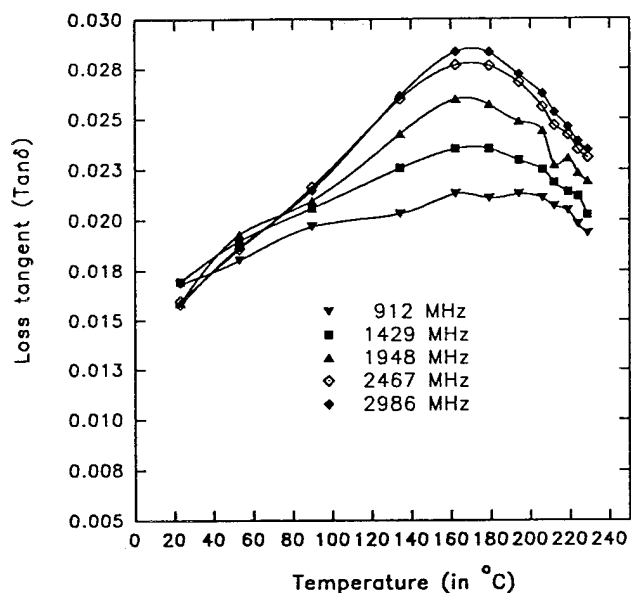


Figure 6. a- The loss tangent of typical PMC samples as a function of frequency and temperature prior to post-cure.

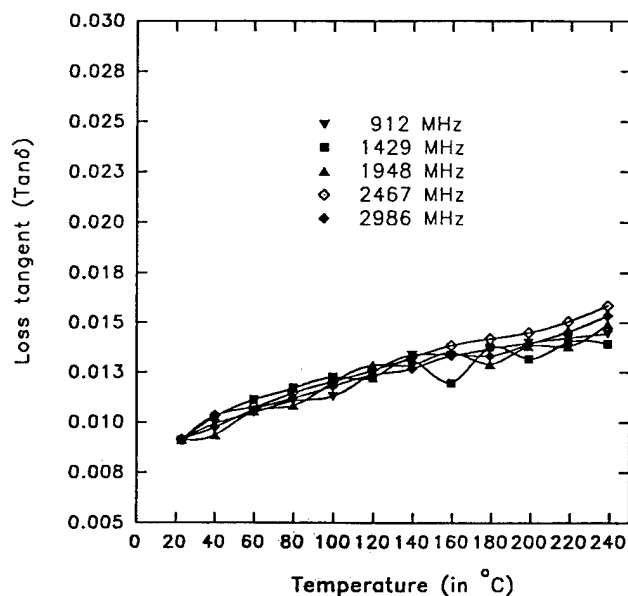


Figure 6. b- The loss tangent of post-cured PMC samples as a function of frequency and temperature.

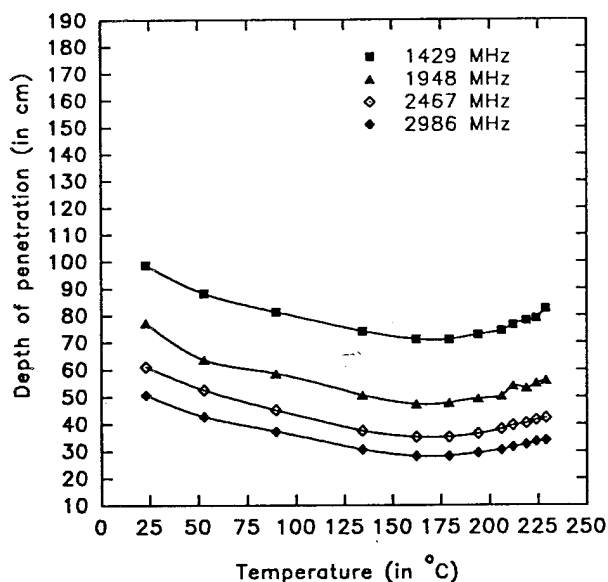


Figure 7.a- The microwave penetration depth as a function of temperature for different frequencies prior to post-cure.

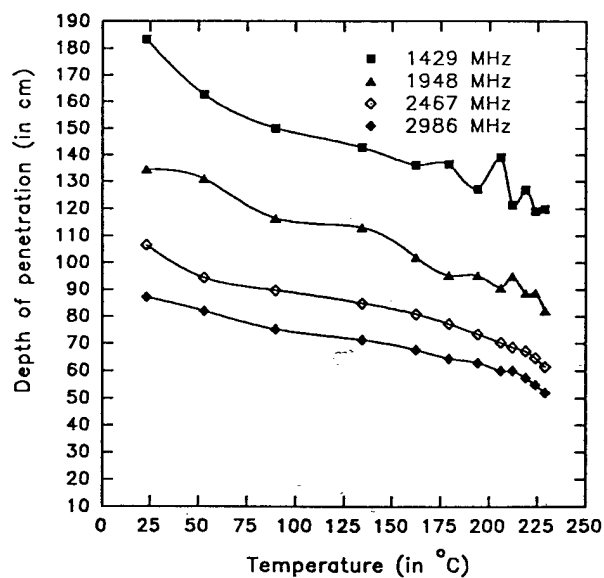


Figure 7.b The microwave penetration depth as a function of temperature for different frequencies for post-cured PMCs.

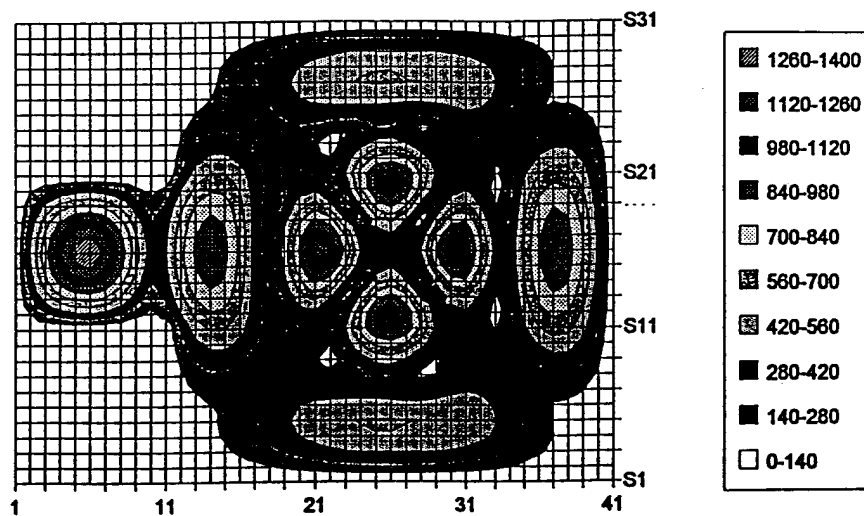


Figure 8.a- The square modal pattern corresponding to 2.45 Ghz resonant frequency(with specimen).

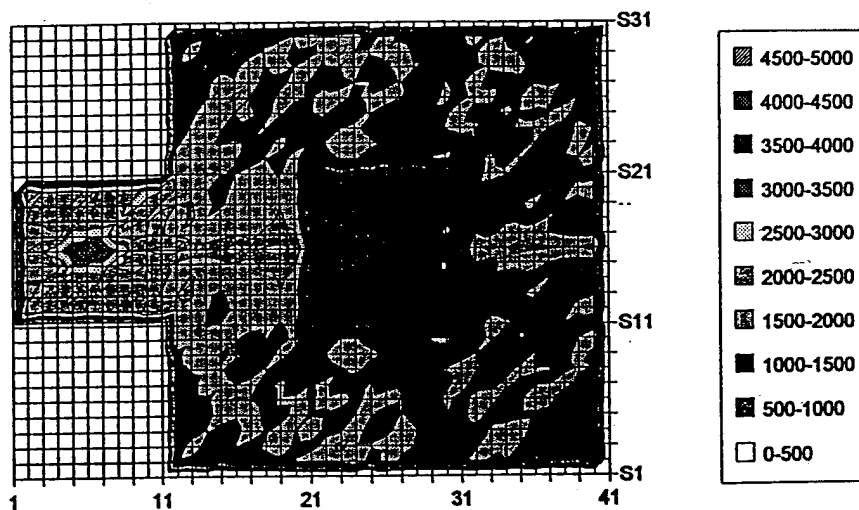


Figure 8.b- The simulation results when the frequency is swept $\pm 10\%$ of the resonant frequency (with composite specimen). **Uniform** electric field distribution is achieved throughout sample volume in the case of variable frequency microwave irradiation.

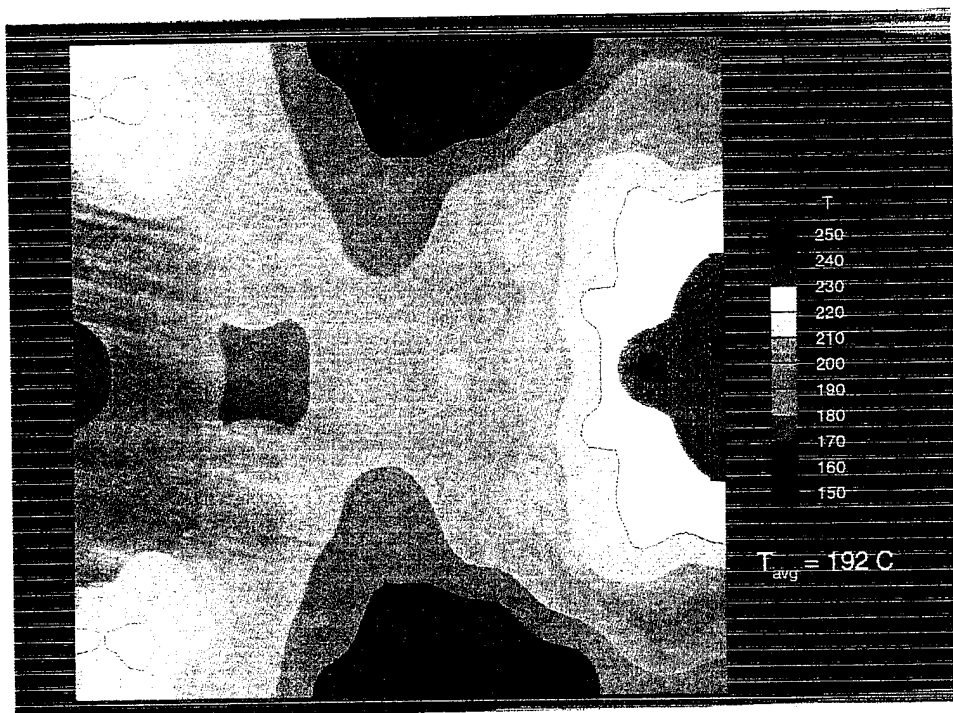


Figure 9.a The simulated thermal profile of a PMC plate irradiated with fixed frequency microwave energy. The average temperature of the sample is 192 C while the temperature gradient exceeds 90 C. The changes in the dielectric constant and the dielectric loss factor as a function of temperature were taken into account.

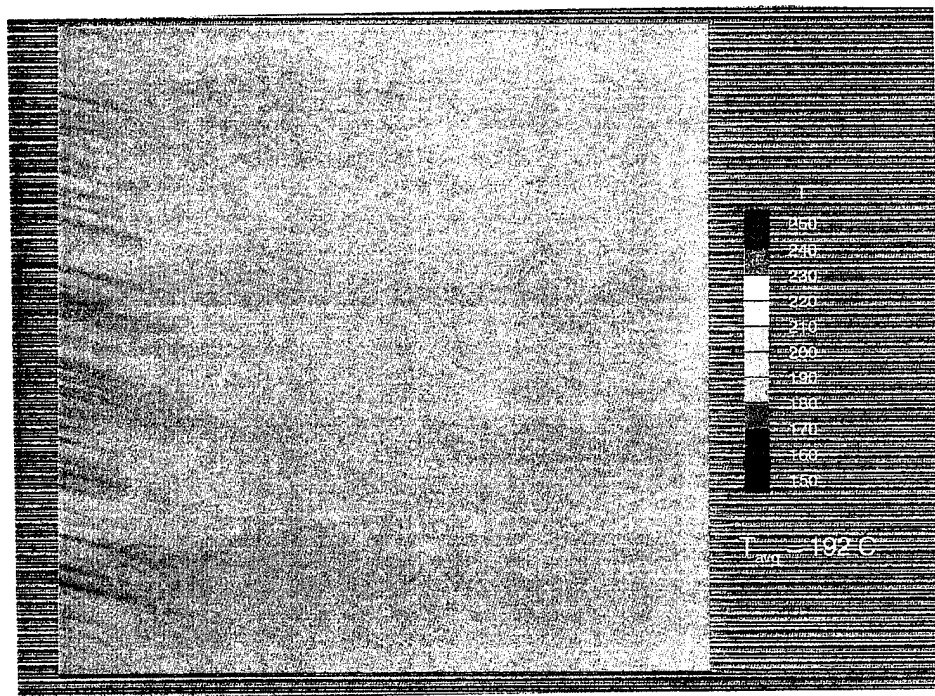


Figure 9.b The simulated thermal profile of a PMC plate irradiated with variable frequency microwave energy. The average temperature of the sample is 192 C, the numerically derived temperature gradient is less than 11 C. The changes in the dielectric constant and the dielectric loss factor as a function of temperature and frequency were taken into account.

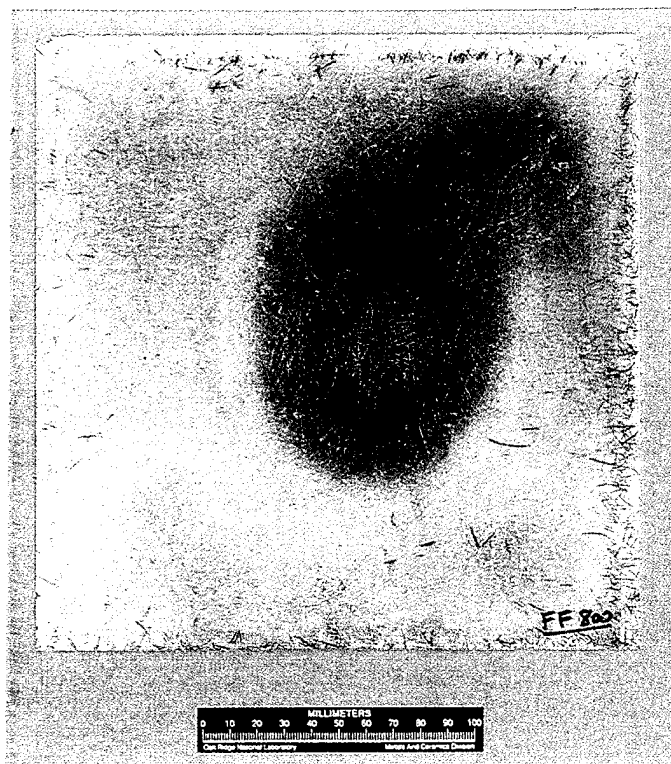


Figure 10.a- PMC samples processed using fixed frequency microwave energy.

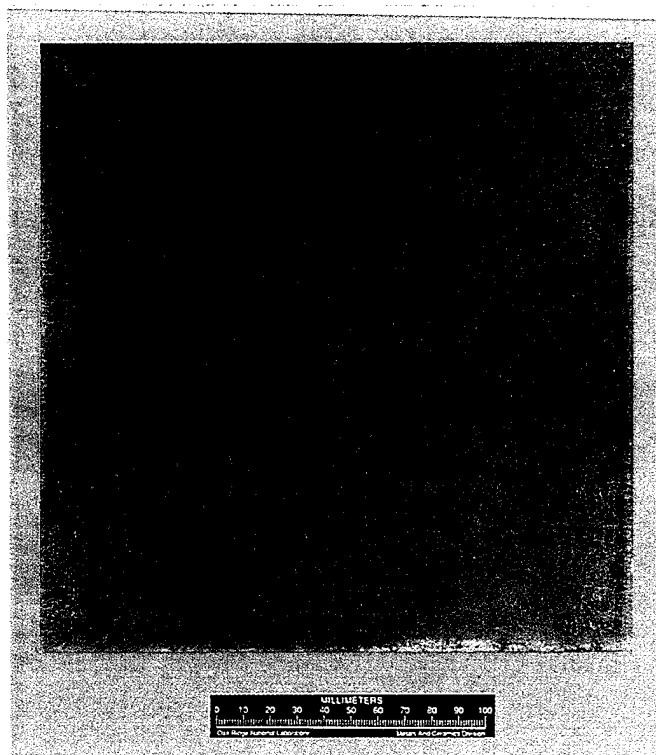


Figure 10.b- PMC samples processed using variable frequency microwave energy.

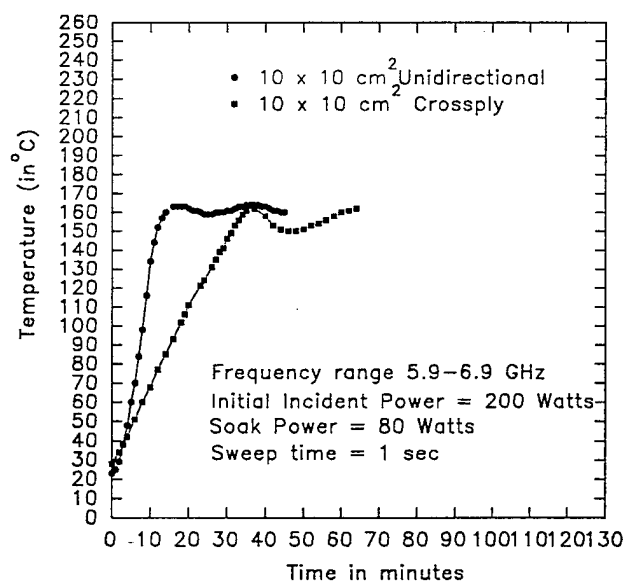
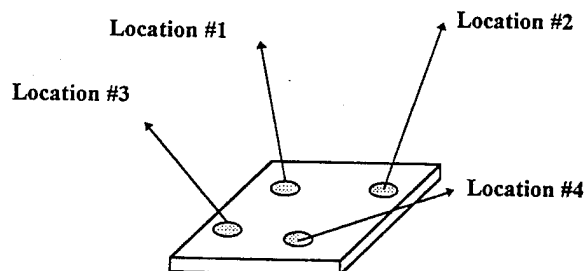


Figure 11.a Temperature profiles of unidirectional and crossply graphite fiber composites during variable frequency microwave heating using



Crossply Graphite fiber reinforced epoxy	
T _g at different locations	
Location#	T _g (°C)
Location#1	181
Location#2	188
Location#3	186
Location#4	181

Figure 11.b Glass transition measurements as a function of location in a representative graphite reinforced composite processed variable frequency microwave energy.

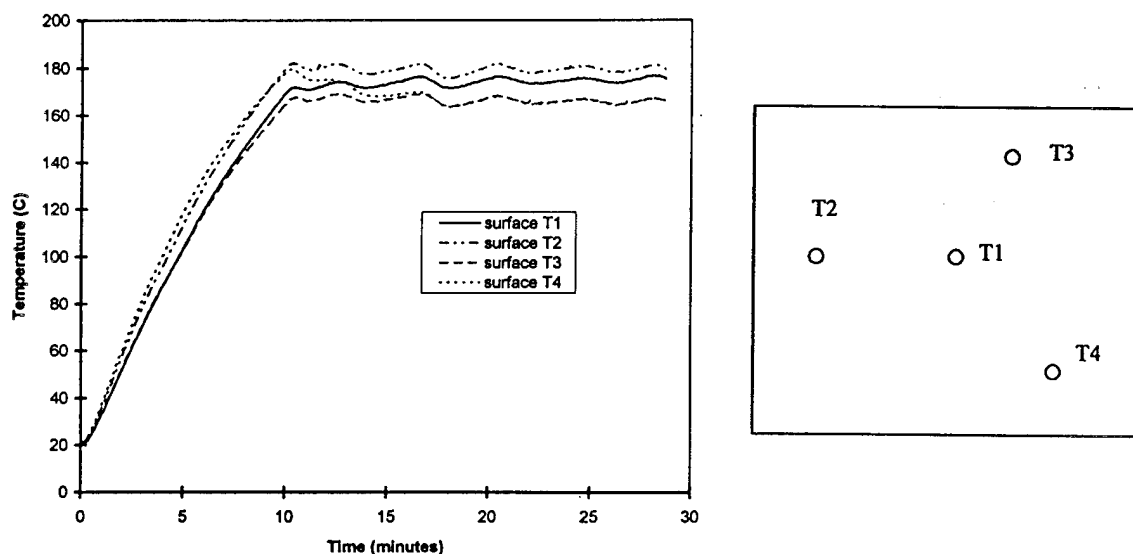


Figure 12. A typical thermal profile generated within unidirectional carbon fiber composites. The temperature was monitored at different locations within the sample as is illustrated in the accompanying Figure.

Process Temp (°C)	G'' peak (°C) dyn/cm ²	G' (knee of the curve) dyn/cm ²
170	200.5	183.6
"	202.6	185.2
"	200.6	184.6
"	205.5	187.9
"	200.5	185.5
"	200.6	184.8
"	200.6	184.0
"	200.7	184.0
"	200.6	182.0

Table 2. Illustrates the G' and G'' for various unidirectional graphite reinforced epoxy composites. Further mechanical testing will be performed to evaluate the mechanical properties of the samples processed using variable frequency microwave energy.

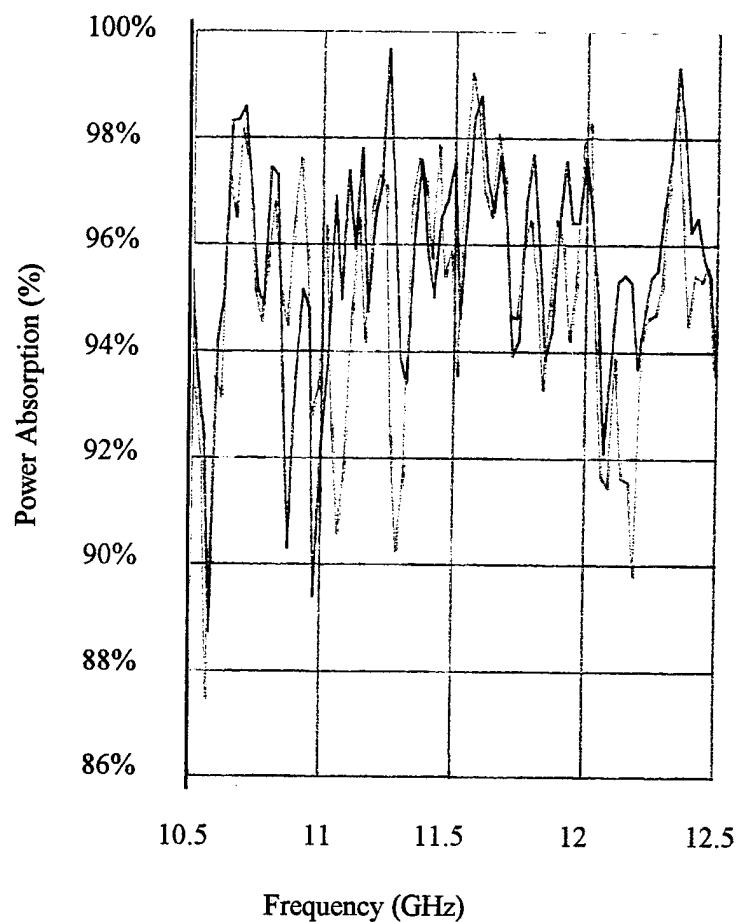
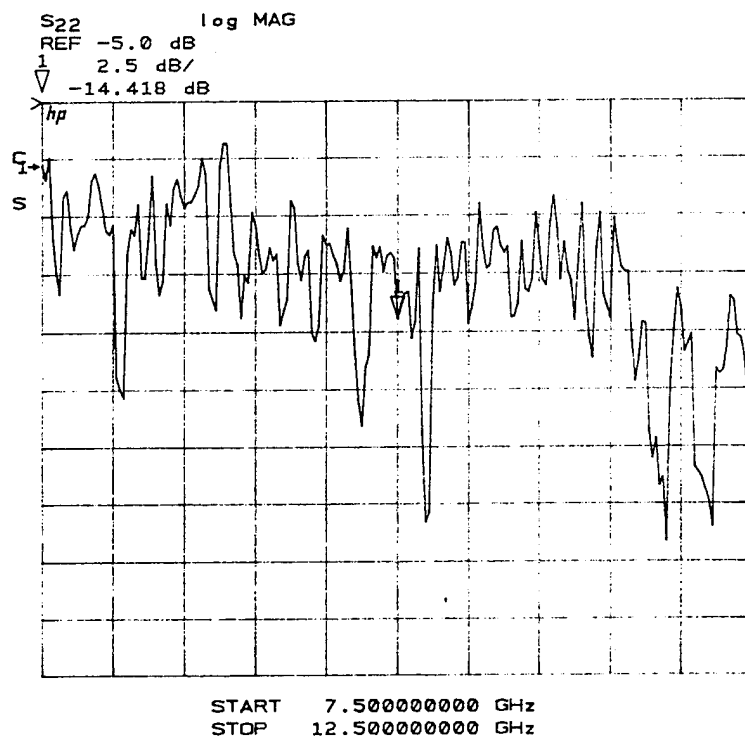
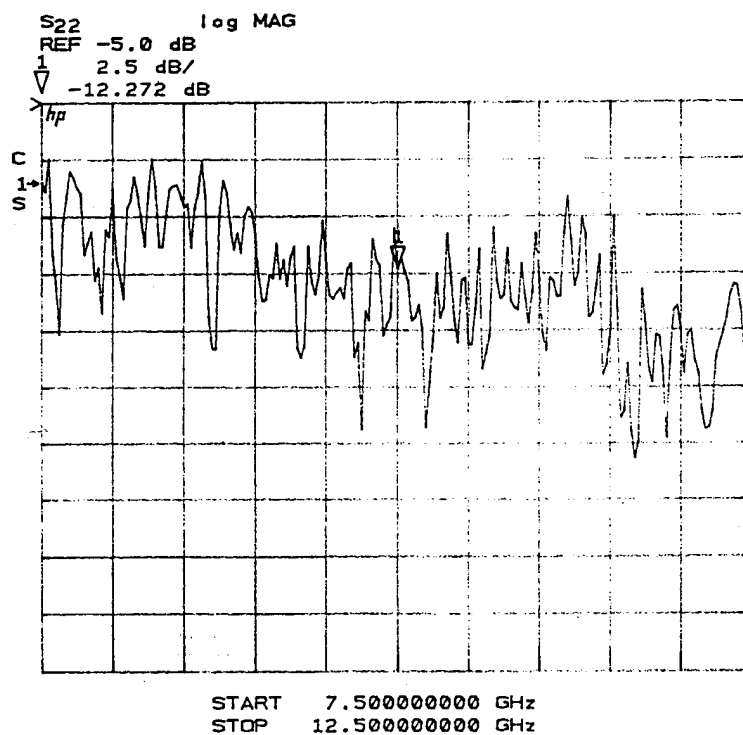


Figure 13- The shift in the characteristic peaks during variable frequency microwave heating of an epoxy resin. The black curve represents the signature of the uncured resin, the red curve represents the characteristic peaks of the fully cured resin.



(a)



(b)

Figure 14. Illustration of the characteristic peaks of glass reinforced isocyanate/epoxy composites during postcure: a- at the beginning of postcure and b- at the end of postcure.